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A New Experimental Method for Measuring Gas Solubilities in Nonvolatile Liquid Mixtures

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A new experimental method for measuring the solubility of a gas in a nonvolatile liquid mixture without analysis of the phase composition is presented. The measured solubility and saturated density for the systems containing carbon dioxide, tridecane, and tetradecane were successfully correlated by an equation of state.

1. Introduction

A new experimental apparatus and method for measuring binary vapor–liquid equilibria at high pressures were proposed in our previous study¹⁾, based on a mass balance and phase rule. The method does not need any analysis of its phase composition. The saturated vapor and liquid densities were separately measured with density meters.

In the present study, a new experimental method is proposed for obtaining the solubility of a gas in a nonvolatile liquid mixture without analysis of its phase composition, and the solubilities of carbon dioxide in tridecane, tetradecane, and tridecane–tetradecane mixture, and their densities were measured at 313.15 K. These experimental values were successfully correlated by an equation of state previously proposed^{2),3)}.

2. Experimental Principles

The proposed experimental method is based on a mass balance, employing a high pressure cell equipped with two density meters. In the following discussions, the gas and the nonvolatile liquid components are denoted by A and B, respectively.

The summation of weight fractions X_{B^0i} of feed liquid mixture is equal to unity.

$$\sum_i^N X_{B^0i} = 1 \quad (1)$$

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Based on a mass balance, the weights of the feed W_A , W_B are expressed as follows:

$$W_A = Y_A W_V + X_A W_L \quad (2)$$

$$W_B = Y_B W_V + X_B W_L \quad (3)$$

in which,

$$W_V = \rho_V V_V, \quad W_L = \rho_L V_L \quad (4)$$

where, Y , X , W_V , W_L , V_V , V_L , ρ_V , and ρ_L denote vapor weight fraction, liquid weight fraction, weight of vapor phase, weight of liquid phase, vapor volume, liquid volume, vapor density, and liquid density, respectively.

Assuming that the liquid component is completely nonvolatile,

$$Y_A = 1, \quad Y_B = 0 \quad (5)$$

$$X_{Bi} = X_B X_{B^0i}, \quad X_B = 1 - X_A \quad (6)$$

Eqs. (2) to (6) are rearranged to give:

$$W_A = \rho_V V_V + X_A \rho_L V_L \quad (7)$$

$$W_B = (1 - X_A) \rho_L V_L \quad (8)$$

The total volume V_T is expressed as:

$$V_T = V_V + V_L \quad (9)$$

In Eqs. (7) to (9), the unknown parameters are V_V , V_L , and X_A .

The quantity X_A , the gas solubility, is given as:

$$X_A = 1 - \frac{W_B}{\rho_L V_L} \quad (10)$$

where,

$$V_L = \frac{(W_A + W_B) - \rho_V V_T}{\rho_L - \rho_V} \quad (11)$$

$$V_V = \frac{(W_A + W_B) - \rho_L V_T}{\rho_V - \rho_L} \quad (12)$$

Based on Eqs. (10) to (12), the gas solubility can be obtained from the feed weights, W_A and W_B , the total volume V_T , and the densities of the vapor and liquid phases, ρ_V and ρ_L .

3. Experimental

The experimental apparatus is completely the same with that in the previous study¹⁾. The schematic diagram of the apparatus is shown in **Fig. 1**. The main parts of the apparatus are placed in a constant temperature liquid bath controlled to within accuracy of ± 0.01 K. The apparatus is suitable for operation with a maximum temperature of 400 K and pressure up to 20 MPa. The volume of the cell A can be varied from 78 cm³ to 134 cm³ by the displacement of a piston P with a sensitivity in the range of ± 0.01 cm³. The reliability of the volume measurement is estimated to be in the range of ± 1 cm³. The volume of the cell is determined by means of a digital counter connected to the piston A. The behavior of vapor-liquid equilibria in

the cell is observed through the visual glass window W. The present apparatus is equipped with two Anton Paar DMA512S density meters with an accuracy of ± 0.0001 g/cm³, a Ruska 2465-752 air dead weight gage, a Ruska 2480-700 oil dead weight gage, two Ruska 2413-705 and 2439-702 pressure transducers, and a Hewlett Packard 2804A quartz thermometer.

The experimental procedure is almost the same with that of the previous study¹⁾. At the start of an experiment, the variable volume cell is evacuated and then charged with the component gas. Pressure difference between the upper and lower chambers of the cell was eliminated. The temperature and pressure were then measured. The volume of gas was determined with the position of piston P. The amount of charged gas was obtained with the volume and density of gas, density measured with density meter.

Now, the nonvolatile liquid was charged with a hand syringe pump S to the variable volume cell A. The amount of the nonvolatile liquid charged was measured by movement of the hand syringe pump S with a sensitivity of ± 0.01 cm³. Then the vapor and liquid phases were recirculated with recirculation pump C. The apparatus was shaken with a motor to achieve the state of equilibrium. The pressure difference between the upper and lower chambers in the variable volume cell A was eliminated with piston P. After attainment of the state of equilibrium, the densities at vapor and liquid phases, pressure, and temperature were measured, observing the coexistence of vapor and liquid phases through the visual glass window W.

A: Variable volume cell, B: Nitrogen cylinder, C: Circulation pump, D: Density meter, E: Constant temperature liquid bath, F: Gas cylinder, G: Pressure gage, H: Hand pump, N: Air dead weight gage, O: Oil dead weight gage, P: Piston, R: Surge tank, S: Hand syringe pump, T: Pressure transducer, V: Valve, W: Visual glass window.

Fig. 1 Schematic Diagram of Apparatus for Measuring Gas Solubility

The total volume was also determined with the movement of piston P.

4. Experimental Results

The solubilities and liquid densities of carbon dioxide in tridecane, tetradecane, and equi-molar mixture of tridecane and tetradecane, and also densities at both phases, were measured at 313.15 K. Carbon dioxide of 99.999 percent purity was supplied by Nippon Sanso K.K. Special grade tridecane and tetradecane of 99 percent purity were supplied by Tokyo Kasei Co. The physical properties of these materials are given in Table 1.

The experimental gas solubility and liquid

density data obtained at 313.15 K for carbon dioxide-tridecane and carbon dioxide-tetradecane systems are given in Table 2 and shown in Figs. 2 and 3. The experimental data obtained for the system of carbon dioxide with equi-molar mixture of tridecane and tetradecane are given in Table 3 and shown in Fig. 4.

The reliability of the present solubility data is estimated to be within ± 0.001 mole fraction, considering the accuracies of the present apparatus and meters used.

The high pressure phase behavior of carbon dioxide-heavy hydrocarbon systems had been reported by some researchers. The critical and three-phase behaviors of carbon dioxide-tridecane system had been reported by Enick *et al.*⁴⁾, Fall *et al.*⁵⁾, and Hottovy *et al.*⁶⁾. The phase densities and vapor-liquid-liquid equilibria for carbon dioxide-tetradecane system also had been investigated by Hottovy *et al.*⁶⁾, Gasem *et al.*⁷⁾, and van der Steen *et al.*⁸⁾. A comparison of the present experimental data with the reported values in literatures⁴⁻⁸⁾, however, were difficult, because of

Table 1 Physical Properties of Materials Used at 298.15 K

Material	Density [g/cm ³]		Refractive index	
	Exptl.	Lit. ¹⁰⁾	Exptl.	Lit. ¹⁰⁾
Tridecane	0.7527	0.7527	1.4239	1.42346
Tetradecane	0.7592	0.75917	1.4274	1.42685

Fig. 2 Experimental Solubilities and Liquid Densities of Carbon Dioxide in Tridecane Obtained at 313.15 K

Fig. 3 Experimental Solubilities and Liquid Densities of Carbon Dioxide in Tetradecane Obtained at 313.15 K

Table 2 Experimental Solubilities and Saturated Densities for Systems of Carbon Dioxide with Tridecane or Tetradecane Obtained at 313.15 K

P [MPa]	x ₁	ρ _L [g/cm ³]	ρ _V [g/cm ³]	P [MPa]	x ₁	ρ _L [g/cm ³]	ρ _V [g/cm ³]
Carbon dioxide(1)-tridecane(2)				Carbon dioxide(1)-tetradecane(2)			
2.113	0.211	0.7494	0.0397	1.468	0.157	0.7534	0.0261
2.493	0.247	0.7511	0.0478	1.739	0.181	0.7545	0.0317
3.520	0.348	0.7558	0.0723	2.928	0.295	0.7593	0.0573
4.092	0.398	0.7586	0.0865	3.406	0.338	0.7613	0.0688
4.801	0.457	0.7628	0.1073	4.874	0.461	0.7689	0.1093
5.322	0.501	0.7659	0.1246	5.542	0.515	0.7726	0.1319
5.817	0.543	0.7695	0.1436	5.785	0.540	0.7740	0.1416
6.438	0.599	0.7738	0.1704	6.370	0.588	0.7777	0.1666

Table 3 Experimental Solubilities and Saturated Densities for System of Carbon Dioxide with Equi-molar Mixture of Tridecane and Tetradecane Obtained at 313.15 K

P [MPa]	x_1	x_2, x_3	ρ_L [g/cm ³]	ρ_V [g/cm ³]
Carbon dioxide(1)-tridecane(2)-tetradecane(3)				
1.896	0.200	0.400	0.7521	0.0348
2.227	0.228	0.386	0.7534	0.0422
3.578	0.352	0.324	0.7598	0.0732
4.118	0.400	0.300	0.7623	0.0873
4.826	0.460	0.270	0.7662	0.1081
5.508	0.518	0.241	0.7702	0.1311
5.867	0.550	0.225	0.7726	0.1444
6.502	0.604	0.198	0.7769	0.1726

●: This work, —: Calculated by EOS.

Fig. 4 Experimental Solubilities and Liquid Densities of Carbon Dioxide in Equi-molar Mixture of Tridecane and Tetradecane Obtained at 313.15 K

the differences that existed in experimental temperatures and pressures.

5. Correlation by the Equation of State

The gas solubility and the saturated density data were correlated by the three-parameter pseudo-cubic equation of state, previously proposed^{2,3}. The equation of state has three parameters, a , b , and θ . The parameters a_c , b_c , and θ for pure substances can be evaluated solely from the critical properties, P_c , V_c , and T_c . The temperature dependence on the parameter “ a ” and “ b ” were introduced as follows:

$$a = K_a a_c, \quad b = K_b b_c \quad (13)$$

$$\ln K_a = S(1 - \sqrt{T/T_c}), \quad S = 1.1746 + 3.4539 \omega \quad (14)$$

The parameter K_a of carbon dioxide was calcu-

Table 4 Parameters Used in Eq. (13) for Pure Liquid Substances at 313.15 K

Substance	ρ_L [g/cm ³]	P [kPa]	K_a	K_b
Tridecane	0.7421	0.0174	2.48268	0.92432
Tetradecane	0.7487	0.0057	2.65560	0.92994

ρ_L : Experimental values, P : Calculated by Antoine equation with constants from Reid *et al.*¹⁰.

lated from Eq. (14), and the parameter K_b of carbon dioxide was taken to be unity. The parameters K_a and K_b of tridecane and tetradecane, computed from the vapor pressures and the densities at 313.15 K, are listed in Table 4.

In a way similar to the present study⁹ on liquid-liquid equilibria, the following mixing rule was used in the present study:

$$\frac{a}{b} = \sum_i^N x_i \frac{a_i}{b_i} - F \quad (15)$$

For function F , the three-parameter Wilson equation (Wilson¹², Renon and Prausnitz¹³) was adopted.

$$\frac{F}{RT} = -C \sum_i^N x_i \ln \left(\sum_j^N x_j A_{ij} \right) \quad (16)$$

Parameter “ b ” is expressed as:

$$b = \sum_i^N x_i b_i + \Delta b \quad (17)$$

For binary systems, Δb is given as:

$$\Delta b = x_1 x_2 \{B_{12}^0 + B_{12}^1(x_1 - x_2)\} \quad (18)$$

For the carbon dioxide(1)-tridecane(2)-tetradecane(3) system, Δb is given as:

$$\begin{aligned} \Delta b = & x_1 x_2 \{B_{12}^0 + B_{12}^1(x_1 - x_2)\} \\ & + x_1 x_3 \{B_{13}^0 + B_{13}^1(x_1 - x_3)\} \\ & + x_2 x_3 \{B_{23}^0 + B_{23}^1(x_2 - x_3)\} \end{aligned} \quad (19)$$

In Eqs. (18) and (19), subscript “1” denotes the gas and subscripts “2” and “3” denote the nonvolatile components, and the parameters “ B_{23}^0 ” and “ B_{23}^1 ” between the nonvolatile liquid 2 and 3 are taken to be zero.

Parameter “ θ ” is expressed as:

$$\theta = \sum_i^N x_i \theta_i \quad (20)$$

The parameters A_{12} , A_{21} , C , B^0 , and B^1 evaluated from the liquid densities and the solubilities at 313.15 K for binary mixtures are presented in

Table 5 Parameters Obtained from Two Binary Mixtures at 313.15 K

System	C	B ⁰	B ¹	A ₁₂	A ₂₁
Carbon dioxide(1)-tridecane(2)	3.0	-27.1643	13.108	0.8727	0.0489
Carbon dioxide(1)-tetradecane(2)	3.0	-41.2147	15.446	0.7371	0.0383

Table 6 Calculated Results of Solubilities and Liquid Densities of Carbon Dioxide in Nonvolatile Mixtures at 313.15 K with Equation of State

System	Δx ₁ _{av}	Δρ _L _{av}
Carbon dioxide(1)-tridecane(2)	0.006	0.0006
Carbon dioxide(1)-tetradecane(2)	0.003	0.0004
Carbon dioxide(1)-tridecane(2)-tetradecane(3)	0.004	0.0032

|Δx₁|_{av}: Σ|x_{1cal}-x_{1exptl}|/I, |Δρ_L|_{av}: Σ|ρ_{Lcal}-ρ_{Lexptl}|/I, g/cm³. I: Number of data.

Table 5. For the ternary carbon dioxide-tridecane-tetradecane system, the parameters obtained in the binary systems were used in the present calculation, and the interactions between tridecane and tetradecane were neglected.

The calculated results of gas solubility in nonvolatile liquid mixtures and liquid densities obtained with the three-parameter pseudocubic equation of state are shown in **Figs. 2** to **4** for the two binary systems and the ternary system. The calculated deviations between experimental and calculated values are presented in **Table 6**.

6. Conclusions

A new experimental method, based on a mass balance for measuring the solubility of a gas in a nonvolatile liquid mixture, without analysis of the phase compositions, was proposed.

The solubilities and liquid densities of carbon dioxide in tridecane, tetradecane, and in equimolar mixture of tridecane and tetradecane were measured at 313.15 K, and were successfully correlated with the pseudocubic equation of state.

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Nomenclatures

- a : parameter in Eq. (13) [kPa·(cm³/mol)²]
- b : parameter in Eq. (13) [cm³/mol]
- B⁰, B¹: parameters in Eqs. (18) and (19) [cm³/mol]
- C : Wilson parameter in Eq. (16) [-]

- F : function in Eq. (15) [kPa·cm³/mol]
- K_a, K_b: correction factors given by Eq. (13) [-]
- I : number of data [-]
- N : number of components [-]
- P : pressure [kPa]
- R : gas constant [kPa·cm³/mol·K]
- S : parameter in Eq. (14) [-]
- T : temperature [K]
- V : volume [cm³/mol]
- W : weight [g]
- X : liquid weight fraction [-]
- Y : vapor weight fraction [-]
- x : mole fraction [-]
- X_B⁰ : liquid weight fraction in nonvolatile liquid component B [-]
- <Greek letters>
- Δ : excess value [-]
- ρ : density [g/cm³]
- θ : parameter given by Eq. (20) [-]
- A : Wilson parameter in Eq. (15) [-]
- <Subscripts>
- A : gas component
- B : nonvolatile liquid component
- c : critical property
- i, j : components
- L : liquid phase
- V : vapor phase
- T : total amount
- 1, 2, 3 : components

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要 旨

非揮発性液混合物に対するガス溶解度の新しい測定法

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本研究では先に提案した高压相平衡測定装置¹⁾を用いて非揮発性のトリデカン, テトラデカン, トリデカンとテトラデカンの等モル混合物への CO₂ の溶解度と液密度を測定した。**Fig. 1** に本研究で用いた高压相平衡測定装置を示した。実験方法は前報¹⁾とほぼ同様である。測定原理は物質収支より Eqs.(1)~(4)の関係が得られ, ここで, 液混合物は非揮発性と仮定すると Eqs.(5)~(9)が得られ, Eqs.(7)~(9)より Eqs.(10)~(12)のガスの溶解度の関係式が求まる。これらより, ガスと液の仕込み量, 全容積, 気液相の密度を測定すればガスの溶解度が求まる。**Table 1** に純物質の物性を示し, **Tables 2, 3** と **Figs. 2~4** に CO₂-トリデカン系, CO₂-テトラデカン系, トリデカンとテトラデカンの等モル混合物における CO₂ の溶解度と飽和液密度データを示した。CO₂ の溶解度と飽和液密度

の相関には先に報告した擬三次型状態方程式を用いた^{2)~4)}。トリデカンとテトラデカンの補正因子 K_a , K_b は温度 313.15 K の蒸気圧と密度を満足するように決め, **Table 4** に示した。変数 a に対する混合則を Eqs.(15), (16)に示し, 関数 F には三定数型 Wilson 式を用いた。変数 b に対する混合則を Eqs.(17)~(19)に示した。式中のパラメーターを**Table 5** に示した。変数 θ に対する混合則を Eq.(20)に示した。CO₂-トリデカン-テトラデカン系において, トリデカンとテトラデカン間の相互作用は無視し, 計算には 2 成分系混合物から得られたパラメーターのみを用いた。温度 313.15 K における非揮発性液混合物へのガス溶解度と液密度の計算結果を **Figs. 2~4** と **Table 6** に示した。

Keywords

Gas solubility, Carbon dioxide, Liquid density, Paraffin